Biology 3550: Physical Principles in Biology
Fall Semester - 2016

Notes on Thermodynamics II
Reversible Processes and Entropy

I. A quick review

In the first lecture on thermodynamics, we began thinking about interconversions between heat, energy and work, using the expansion of a gas as an example.

We considered three paths from a relatively compressed volume of gas to an expanded volume:

- Adiabatic expansion with no work. $\Delta E = 0$, $q = 0$, $w = 0$
- Adiabatic expansion with work. $\Delta E < 0$, $q = 0$, $w < 0$
- Isothermal expansion with work. $\Delta E = 0$, $q > 0$, $w < 0$, $q = -w$

We emphasized that the internal energy of the system, E, is a state function that is independent of the path leading to the final state. But, q and w, the heat and work associated with a change in state, are path-dependent. The three quantities are linked by the first law of thermodynamics:

$$\Delta E = q + w$$

We also argued that the maximum amount of work obtainable from expanding the gas was gained by requiring that the gas expands very slowly at a constant temperature, so that the temperature of the gas never falls. The pressure will drop continuously as the volume increases, following the gas law. If the temperature does fall temporarily, the pressure will be less than it would be otherwise, and the force is less than it would be otherwise. Thus, less work can be done. During this process, the heat must flow into the system and is converted into work.

The maximum amount of work obtainable from the expansion of the gas is also the *minimum* amount of work that would be required to restore the gas to its original state. In order to compress the gas using this minimum amount of work, the process must be carried out in infinitesimal reversible steps. The argument is simply turned around: If the gas is compressed in finite steps in which the temperature is allowed to increase and then is cooled, the pressure will increase, requiring more work to move the piston the same distance. If the expansion and compression are carried out reversibly, then the system is restored to its original state with no gain or loss in work. But, any deviation from reversibility will lead to the net expenditure of work, or free energy. All real processes involve a loss of available work.

We say that the the slow, isothermal process is reversible in two senses. First, as argued above, reversing the process returns the system to its original state with no net loss or gain of work. The other processes we discussed can be reversed as well, but always at

some cost in work. Second, the process is reversible in that each step can be reversed with an infinitesimal amount of force acting in the reverse direction.

Today, we will actually calculate the maximum amount of work for an isothermal gas expansion and show how it is related to entropy.

II. The maximum work from expanding a gas at constant temperature

We can calculate the work from the reversible isothermal expansion with a bit of calculus, starting with the integral for any work function:

$$w = \int_{x_1}^{x_2} f\,dx$$

where x_1 and x_2 are the initial and final positions of the piston, and f is the force. The force, in turn, is proportional to the pressure at any instant:

$$f = -P \cdot A$$

where A is the area of the piston. The negative sign reflects the fact that the work done on the system by expansion will be negative. For each small increment of x, there is a corresponding small increment in the volume of the gas:

$$dV = A\,dx$$

or, we can write:

$$dx = dV/A$$

We can replace dx in the integral with dV/A, and f with $-P \cdot A$, so that:

$$w = -\int_{V_1}^{V_2} (P \cdot A)dV/A$$

$$= -\int_{V_1}^{V_2} P\,dV$$

(recall that the product PV has the units of energy, or work!) We can also express pressure in terms of volume, $P = nRT/V$:

$$w = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

n, R and T are all constant, so they can be moved outside of the integral.

$$w = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$= -nRT \ln(V)\Big|_{V_1}^{V_2}$$

$$= -nRT \ln\left(\frac{V_2}{V_1}\right)$$

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Since we have the same number of molecules at the beginning and end of the process, the concentration is inversely related to the volume. So, we can write this expression in terms of concentration:

$$w = -nRT \ln \left(\frac{C_1}{C_2} \right)$$

The form of this expression will likely be familiar to you, or will be soon. This is the origin of all of the expressions like $-RT \ln(C_1/C_2)$ that occur so frequently in chemistry!

III. Thermodynamic definition of entropy

The maximum work that we calculated is simply a function of the temperature and the starting and finishing volumes. This is consistent with the suggestion that this quantity can be considered a state function. It also describes what is *lost* when a gas expands, the ability to do work, and it seems to be related to the increased disorder of the gas, *i.e.,* its entropy.

In fact, the thermodynamic definition of entropy is based on the heat absorbed, q, via the path leading to maximum work:

$$\Delta S = \frac{q_{rev}}{T}$$

where q_{rev} is the heat absorbed by the system in the reversible process, which is $-w_{rev}$.

This was easiest to describe for a process in which the temperature stayed constant, but there is still a maximum amount of work that can be obtained for the transition between two states that have different temperatures, and this maximum amount of work is obtained through a reversible, (*i.e.,* infinitely slow) path. In this case, the entropy change is calculated as an integral:

$$\Delta S = \int_{T_1}^{T_2} \frac{q_{rev}}{T} dT$$

where T_1 is the initial temperature and T_2 is the final temperature, and q_{rev} may be a continuously changing function of temperature.

Now, entropy is supposed to be a quantity that increases spontaneously and is related to disorder. In the case of the expanding gas, the quantity we calculated above does seem to be related to disorder, since the molecules are less ordered in a larger volume.

The entropy of a system, as defined here, is a state function. The entropy changes by the same amount irrespective of how much work, for instance, was obtained from the expansion.

But, it is important to point out that this definition only applies to the isolated system. We haven't said anything about how the entropy of the surroundings change. We will come back to this when we talk about the second law, which concerns the entropy of the system *and* its surroundings.

IV. The statistical interpretation of entropy

The classical definition of entropy is probably not the one that you are most familiar with, which probably refers to the idea of randomness or disorder. In fact, the classical definition is is not an easy concept to work with and is only useful in rather restricted cases, like heat engines.

The important point from the previous discussion is that the energy, E, is a function that helps define a state, but the change in energy for a change from one state to another is not sufficient to tell us whether or not the change is favorable or how much work can be obtained. In addition to the internal energy, there is this other quantity that defines the states and determines how much work can be obtained.

In the case of the expanding gas, it appears that the driving force is the tendency of the individual molecules to occupy as large a volume as is made available to them. As we have repeatedly discussed, this is a purely probabilistic phenomenon. If the molecules begin on one side of the container and are allowed to move freely to the other, there is a 50% probability that any one molecule will wind up on the other side. There will be a net flow to the other side until the concentrations on the two sides are equal.

The statistical definition of entropy of a state can be expressed as:

$$S = k \ln \Omega$$

where k is the Boltzmann constant, and Ω is the number of equally probable microstates that make up the state. In other words, Ω is the number of different ways of arranging the components of the system. This is the fundamental postulate of statistical mechanics. It was deduced (not proven!) by Ludwig Boltzmann, and it is engraved on his tombstone in Vienna. Like the laws of thermodynamics, we believe it because it works!

So, all that we have to do to calculate the entropy is count up the ways of arranging the components. How do we do *that*?

This is not at all trivial, and all we can usually do is apply this definition to idealized simple systems. But, the problem is made a little bit easier if we only try to calculate the *change* in entropy a process. For instance, we can go back to our example of a gas expanding. For even a modest number of molecules, there is a vast number of microstates, each defined by the position and momentum of each molecule. We obviously can't count them all. But, if the temperature stays constant, then the number of possible values for the momentum of each molecule stays the same. So, that all we have to consider is the number of different positions for each molecule.

Suppose that we divide up the initial volume into a grid of small cubes, say $1\,\mathrm{nm}$ on a side. If the number of molecules is N and the number of cubes is M, then we can calculate the number of ways of arranging the N molecules into the M cubes. To simplify things, we can assume that M is much larger than N, so that once we place a molecule in a given cube, it doesn't significantly reduce the number of places available to the next molecule. So, taking one molecule at a time, the number of ways

of arranging them is:

$$M \cdot M \cdot M \cdots = M^N$$

But, if all of the molecules are indistinguishable, then we have to divide by number of ways of choosing the molecules sequentially, $N!$. So:

$$\Omega = \frac{M^N}{N!}$$

So, the initial entropy would be:

$$S = k \ln \Omega = k \ln \left(\frac{M^N}{N!} \right)$$

But, this is a little suspect, since the result depends on the number of cubes that I divided the volume up to. Would the entropy suddenly become larger if I decided to use smaller cubes? That doesn't sound right. But, it turns out to be OK if we consider a *change* in volume.

If we call the initial number of cubes M_1 and the final number M_2, the change in entropy is given by:

$$\Delta S = S_2 - S_1 = k \ln \left(\frac{M_2^N}{N!} \right) - k \ln \left(\frac{M_1^N}{N!} \right)$$

$$= k(N \ln(M_2) - \ln(N!)) - k(N \ln(M_1) - \ln(N!))$$

$$= kN \ln \left(\frac{M_2}{M_1} \right)$$

If we want to express this on a molar basis, n, the number of moles, is equal to N divided by Avogadro's number, N_A, and $N = nN_\mathrm{A}$:

$$\Delta S = nN_\mathrm{A} k \ln \left(\frac{M_2}{M_1} \right)$$

Since k is the gas constant, R divided by Avogadro's number, we can write:

$$\Delta S = nR \ln \left(\frac{M_2}{M_1} \right)$$

Finally, M_2 and M_1 are proportional to the volumes before and after and we can write the expression as:

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

Notice that this is exactly equivalent to the classical definition of the entropy change for this process:

$$\Delta S = \frac{q_{rev}}{T} = \frac{-w_{max}}{T}$$

$$= \frac{1}{T}nRT\ln\left(\frac{V_2}{V_1}\right) = nR\ln\left(\frac{V_2}{V_1}\right)$$

Notice also that if we use smaller cubes, the values of M_2 and M_1 are larger, but the difference cancels out.

V. Entropy and information

There is another way of thinking about entropy that comes from a quite different discipline, information theory, which is concerned about how to efficiently and accurately transmit and manipulate information. This was a subject that was developed during the middle decades of the 20th Century, largely at the late great Bell Laboratories, which did basic research for the major U.S. telephone company of the time (AT&T).

In this view, entropy can be described as the amount of information required to specify the exact state of a system. So, for instance, a crystal of a pure substance can be described with relatively little information, because each molecule is in an equivalent position of the crystal. If we know the structure of the molecule and the parameters describing the crystal lattice, then we can completely reconstruct the structure of the crystal. On the other hand, to completely describe a gas of the same molecules requires that we individually specify the position and momentum of each molecule.

This idea can be quantified, to give a function that calculates, for instance, the number of bits required to transmit a particular message or other information such as images or audio signals. Some messages contain a great deal of repetition and so can be encoded with relatively few bits, meaning that they have low entropy. A message composed of randomly-chosen letters has a high entropy and requires more bits to communicate. The equations for calculating information content have exactly the same form as the statistical definition of thermodynamic entropy, and information content is often described as information entropy.

The science of information theory has become very important in the digital age, as it defines the minimum amount of resources (including time) required to transmit a message or other information. The algorithms that are used to compress computer files, images and mobile-phone transmissions take advantage of the fact that the information is *not* random, *i.e.,* has a relatively low entropy, to represent it with less data.

There is another interesting aspect to the relationship between information and entropy. Reducing thermodynamic entropy requires work, or energy. Similarly, manipulating information and reducing its entropy (such as in compressing it) requires work. There are people working on the theory of quantifying exactly what is the minimum amount of energy required for specific computational tasks.

We don't always think about it, but the information technologies that we take advantage of use huge amounts of energy. Google is a major energy consumer. In 2009, the

London Times published an article saying that a Google search produced about 1 g of CO_2, and this number is widely cited. This claim was quickly denied by Google, which a couple of years later released its own estimates of its energy consumption, indicating that a single search uses 0.3 watt h (the energy required to power a 60-watt light bulb for about 20 s, or 3,600 J). If produced by burning coal, this would produce about 0.2 g of CO_2, far less than the original estimate. To its credit, Google has also invested heavily in renewable energy sources.